

STRUCTURAL CHARACTERISTICS AND SWELLING MECHANISM OF TWO COMMERCIAL NITRILE-BUTADIENE ELASTOMERS IN VARIOUS FLUIDS

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ABSTRACT

Results on the structural characteristics and swelling mechanisms of the two commercial elastomers viz. N0674-70 and peroxide cured N0741-75 in a variety of fluids are reported here. The fluids used in these investigations included toluene, o-xylene, p-xylene, mesitylene, HISOL-15, n-hexane, ethanol, tert-butyl alcohol, acetone, JP-8, S-8 and blends of S-8 plus HISOL-15 and S-8 plus toluene. Both changes in mass and volume of the rectangular disks of the samples were monitored as a function of time. Structural characterization of the elastomer was done using x-ray diffraction and FTIR spectroscopy. Time dependence of the recovery of swelling after the elastomers are taken out of the fluids was monitored by x-ray diffraction and changes in mass. In general swelling of the peroxide cured N0741-75 was less than that of N0674-70, percentage changes in mass were less than the percentage changes in volume, and the swelling is strongly fluid dependent.

For initial times, the swelling is interpreted in terms of diffusion of the fluid into the elastomer. However, diffusion is not strictly Fickian in that the exponent differs from 0.5 for Fickian diffusion, instead varying between 0.4 and 0.6 for different fluids. It is shown that the results of maximum swelling can be interpreted in terms of compatibility of the Hansen Solubility Parameters (HSP's) of the fluid and the elastomer, swelling decreasing on a Gaussian curve as the HSP of the fluid deviates from that of the elastomer. Also, swelling is determined by the polybutadiene component of the elastomer. In HISOL-15, a commercial aromatic solvent, nitriles swell by about 55% and mixing of HISOL-15 with S-8 produces swelling linearly proportional to the % of mixed HISOL-15. The observed few percent decrease in swelling on long-term exposure may be related to loss of material and so eventual failure of the nitrile O-rings.

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1. Introduction

The engines in most of the modern transportation vehicles used in the civilian and military sectors are designed for fuels derived from the conventional petroleum crude oil. These fuels contain a certain percentage of aromatics and sulfur which provide lubricity and the desired amount of elastomer swelling of the O-rings to prevent fuel leaks. The synthetic fuels produced by Fischer-Tropsch synthesis, if used in such engines, will have to be blended by appropriate additives to achieve the desired amount of lubricity and elastomer swelling. Therefore it is highly desirable to investigate and understand the swelling characteristics of commercial level elastomers in different fluids.

Nitrile rubber elastomers are copolymers of polyacrylonitrile, $-(\text{CH}_2=\text{CH}-\text{C}\equiv\text{N})_n$ and polybutadiene, $-(\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2)_n$. The characteristics of a given elastomer are therefore expected to depend on the percentages of these two primary components in the elastomer. In recent years, results from a number of investigations have appeared in literature [1-5] in which the authors have varied the relative compositions of these two components in laboratory prepared samples and investigated their swelling characteristics in aromatics such as benzene, toluene and xylene. These studies have provided considerable insight into such factors on the role of molar volume of the fluid on its diffusion into specimens of various compositions [1-5].

The commercial elastomers such as O-rings usually contain additional components such as plasticizers, fillers and curing agents in addition to polyacrylonitrile and polybutadiene. In addition, the relative percentages of these components in a given elastomer are usually a trade secret and not known accurately. A few years ago, Muzzell et al [6] carried out investigations of the swelling and compatibility of three commercial elastomers (see Table 1) in synthetic S-5 fuel blended with various percentages of the commercial A-150 aromatic solvent and in JP-5/JP-8 aviation fuels. In these investigations, magnitudes of the saturation swelling achieved after several days of immersion in a fluid was the primary focus of attention. This work was followed up by investigations by Graham et al [7] on the swelling characteristics of commercial nitrile O-rings in selected aromatics blended in synthetic jet fuel.

The present study was undertaken to investigate the swelling characteristics of the same there elastomers (Table 1) as used in the work by Muzzell et al [6] with a goal to reach a more fundamental understanding of how saturation is achieved in different fluids and how it depends on the characteristics of the fluids. For this purpose, we have used a variety of fluids, both

aromatics and alkanes and measured the time dependence of changes in mass and volume of the elastomers. The obtained results are discussed in terms of diffusion phenomenon and on the properties of the fluids such as their molar volumes and their Hansen Solubility Parameters (HSP) [8]. Results on the swelling characteristics of the elastomers in thirteen different fluids and fluid blends are reported. The compatibility of the HSP's of an elastomer and a fluid are shown to control the swelling observed in a given fluid. Details of these results and discussion are presented in the following pages.

2. Experimental Procedures

2.1 Materials

In our research work, two commercially available elastomers viz. N0674-70 and peroxide cured N0741-75 from Parker Co. were studied. A third elastomer V0884-75 was also studied initially, but no further experiments were conducted on it as this fluorocarbon (V0884-75) did not show any significant change in mass or volume when immersed in a solvent. Consequently no data on V0884-75 is reported here. The descriptions of the elastomers used in our work are shown in Table 1 [6].

Table 1: Elastomers investigated in this work.

Elastomer Name	Elastomer Description
N0674-70	70-durometer nitrile, general purpose
N0741-75	75-durometer nitrile, peroxide cured
V0884-75	75-durometer fluorocarbon, non-black filled

The two nitrile elastomers contain polyacrylonitrile and polybutadiene in various proportions in addition to fillers to provide strength to the elastomers. These elastomers are typically found in some fuel systems of Army tactical and combat vehicles [6]. The solvents used for the experiments were toluene, o-xylene, p-xylene, mesitylene, HISOL-15, n-hexane, ethanol, tert-butyl alcohol, acetone, JP-8, S-8 and blends of S-8 plus HISOL-15 and S-8 plus toluene. HISOL-15, a universal aromatic solvent, was kindly provided by SHELL Co. and JP-8 and S-8 were obtained through the courtesy of Pat Muzzell. All other fluids were purchased from commercial sources (Alfa Aesar).

2.2 Procedures for measuring swelling:

From the available elastomers coupons, small rectangular disks were cut by means of a sharp edged knife. The thickness, length and width of the disks were measured using a vernier caliper with an accuracy of ± 0.01 mm with typical dimensions of samples being about $10 \times 10 \times 2$ mm³. All measurements were done at room temperature. For mass changes, we followed the ASTM D471 method using a sensitive balance with an accuracy of ± 0.1 mg. These rectangular disk-shaped samples were immersed in about 20-30 ml of the solvent in small glass test bottles. To measure changes with time, the immersed samples were periodically removed from the glass bottle, the solvent on the elastomers was wiped off quickly using wipes, and the sample was then weighed using the sensitive balance. The dimensions of the sample were measured using the vernier caliper and the results were recorded. After measuring the weight and the dimensions, the elastomer is immediately placed back in the bottle with the solvent. The time taken for each set of measurements was kept to a minimum and was approximately 50-60 seconds. This procedure was continued until no change in the weight and volume was observed in the elastomer i.e. until the elastomer swelling reaches saturation.

3. Structural Characterization of Elastomers

3.1 Fourier Transform Infra-red Spectroscopy (FTIR)

The primary area of focus was acquiring IR spectra of the two elastomer samples using FTIR spectroscopy to study the chemical structure of the species present in the samples. A Mattson Infinity Gold FTIR spectrometer was used to obtain the IR spectra. The IR spectrum of polybutadiene and raw polyacrylonitrile butadiene sample was also acquired to examine how different the chemical structure of the commercially available elastomer is when compared to the pure elastomer sample. Techniques of attenuated total reflectance (ATR), photoacoustic spectroscopy (PAS) and transmission spectroscopy using standard KBr method were tried to obtain the best signal to noise IR spectra. For PAS and KBr methods, the samples were powdered using laboriously hand grinding the samples on a plane white paper to obtain very fine powder of these difficult-to-grind polymers.

The IR spectra of polybutadiene and raw polyacrylonitrile butadiene are shown in Fig. 1. These spectra were obtained by using ATR. A prominent feature of polyacrylonitrile butadiene is the presence of the nitrile (cyano) $\text{-C}\equiv\text{N}$ group which is known to yield a sharp peak at 2235 cm^{-1} in IR spectra. The presence of the line due to $\text{C}=\text{C}$ double bond near 1640 cm^{-1} is noted along

with significant peaks near 1440 cm^{-1} and 969 cm^{-1} due to C-H bond in the butadiene part of the nitrile rubber.

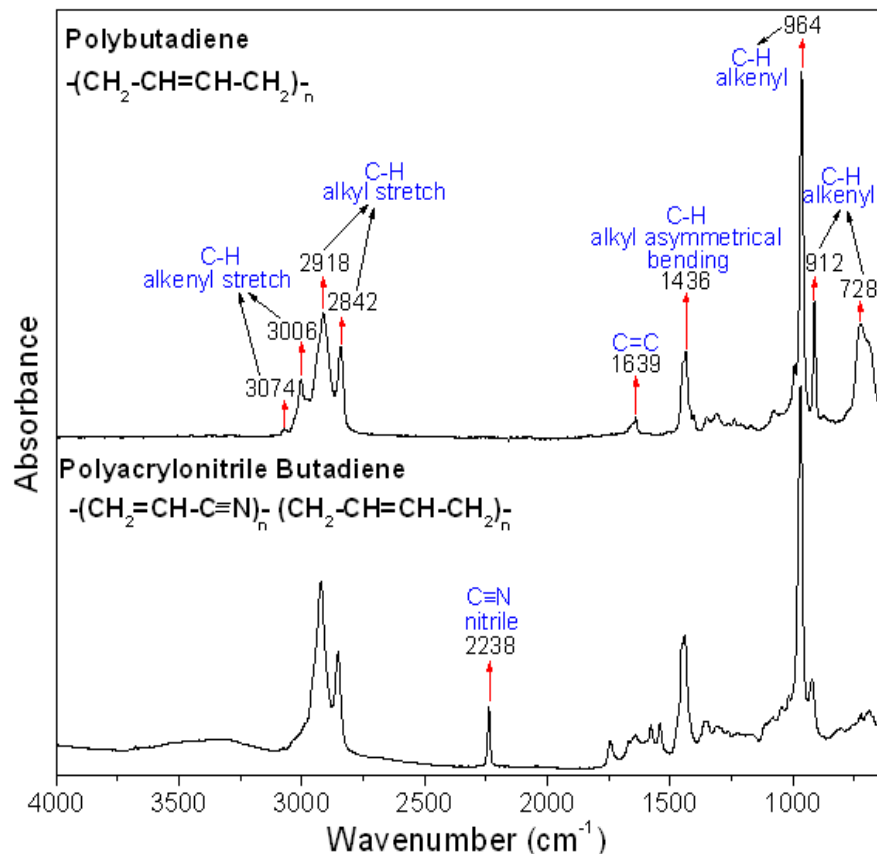


Figure 1: IR spectra of Polybutadiene and raw Polyacrylonitrile Butadiene acquired using ATR technique.

Techniques of photo-acoustic spectroscopy (PAS), attenuated total reflectance (ATR) and KBr-pellet transmission spectroscopy to acquire the IR spectra of the elastomer samples were tried. Since PAS spectra were noisy, we tried ATR which can be done on solid samples also, although powdered samples yield better spectra. In terms of signal to noise ratio, we found the KBr pellet method to be the best for our purpose. The IR spectra of the nitriles N0674-70 and N0741-75 obtained using KBr pellet method are shown in Fig. 2. In the IR spectra of both elastomers, the nitrile ($\text{-C}\equiv\text{N}$) band at 2235 cm^{-1} is barely noticeable. This could be due to the presence of additives/fillers in the elastomers and the curing of commercial nitriles. The near absence of the cyano group IR band in commercial elastomers also suggests its involvement in crosslinking. The broad band near 3300 cm^{-1} in the commercial nitriles is likely due to absorbed water.

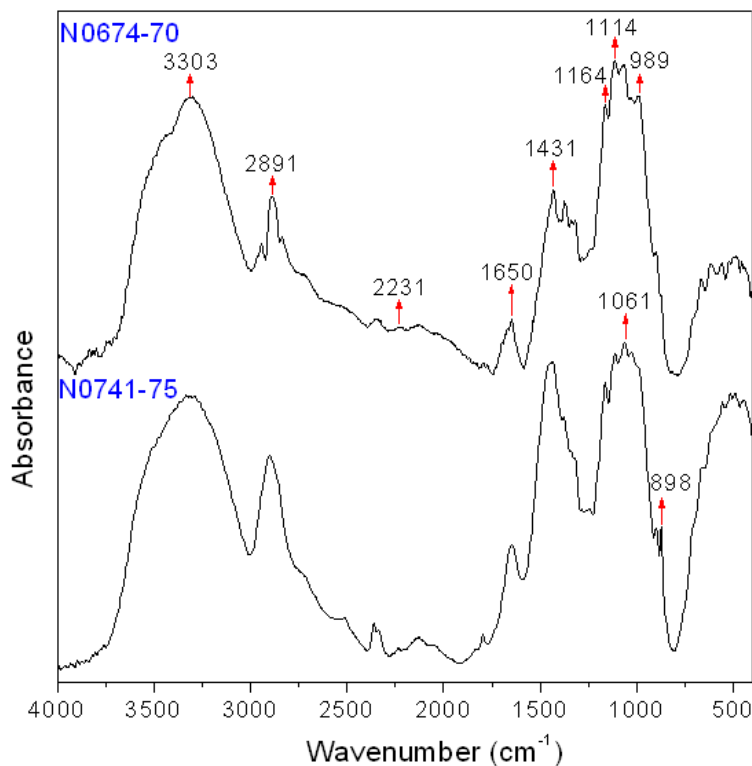


Figure 2: IR spectra of N0674-70 and N0741-75 obtained using KBr pellet method.

3.2 X-ray Diffraction (XRD)

To study the swelling process at the microscopic level, x-ray diffraction (XRD) studies were carried out on the two elastomer samples, N0674-70 and N0741-75, for three cases: (i) as-received samples, (ii) samples immersed in toluene overnight and (iii) the same sample in (ii) aired for several days. Room temperature wide angle XRD scans of these samples were carried out using a Rigaku (D-Max) diffractometer and CuK_α source with wavelength $\lambda=0.15418$ nm.

The x-ray diffraction pattern for N0674-70 as received, exposed to toluene and aired is shown in Fig. 3. Similar data for N0741-75 is shown in Fig. 4. The sharp peaks observed in the XRD pattern of N0674-70 are easily identified with crystalline ZnO. ZnO is a well-known promoter for cross-linking in elastomers [8]. The lattice constants of ZnO present in N0674-70 is however smaller by about 2% possibly by some internal compression in N0674-70 as compared to the XRD spectra of standard ZnO. The broad peak near 22° is likely due to non-crystalline polymer with its second order satellite clearly evident near 44° . For the peroxide cured N0741-75 sample, the peaks are tentatively identified with the promoters, oxide and sulfides of Ti ($\text{TiO}_{1.04}$, TiS and Ti_3S_4). All the sharp peaks nearly disappeared after swelling by about 120% in toluene but the peaks were recovered after swelling was reversed on airing the sample. It is possible that

during the swelled state, toluene present inside the elastomers blocks ZnO and the crystalline Ti-compounds being exposed to x-rays resulting in disappearance of the sharp lines although we are not certain of the exact causes of the disappearance of the lines in the swelled state.

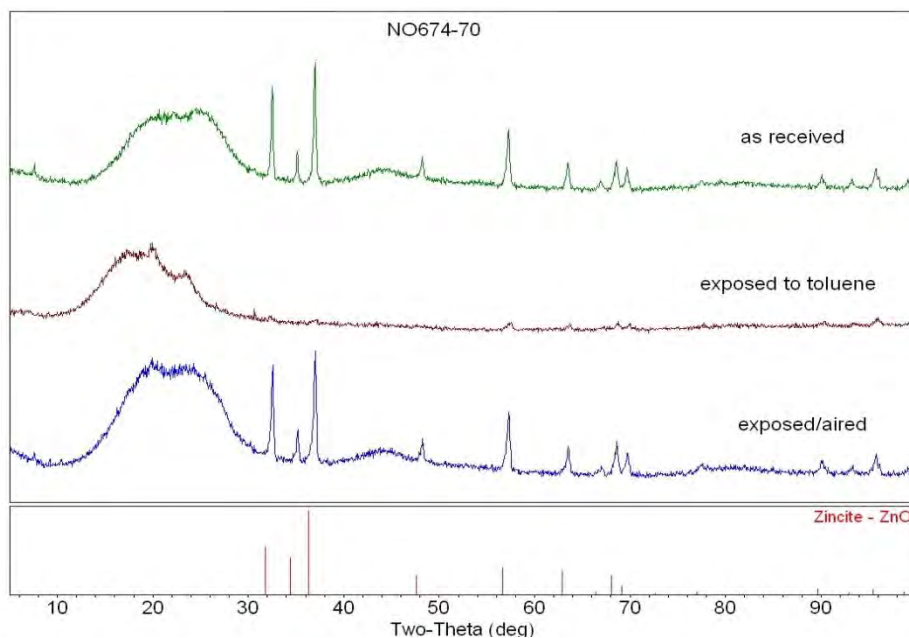


Figure 3: X-ray diffraction pattern of N0674-70 and line positions of ZnO.

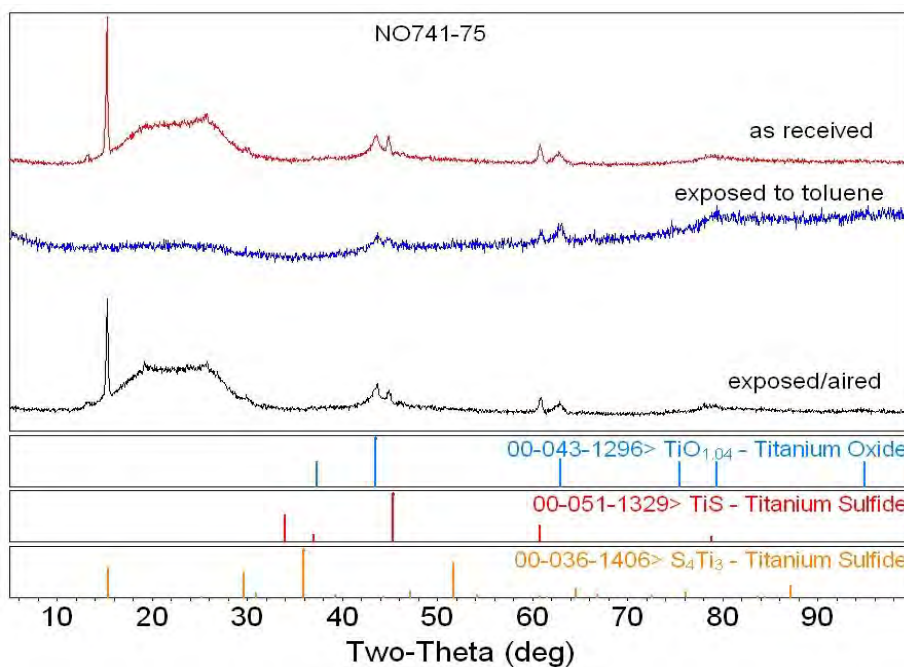


Figure 4: X-ray diffraction pattern of N0741-75.

As the swelled material is exposed to air, the ZnO spectra slowly recovers with time as toluene escapes and the elastomer returns to near original state as shown in Fig. 5. By measuring change in the intensity (area A under the peak) of an XRD line with time, we have fitted the data to the exponential recovery equation:

$$A(t) = A(0) [1 - \exp(-t/t_s)] \quad (1)$$

with $t_s = 60$ minutes, although complete recovery requires over 300 minutes. The fitted data is shown in Fig. 6.

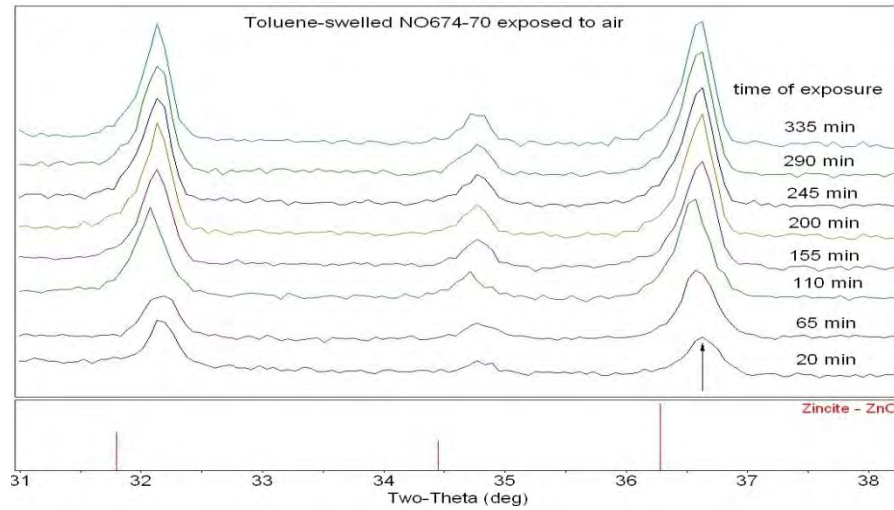


Figure 5: Increase in intensity of the ZnO XRD lines of the swelled nitrile on exposure to air.

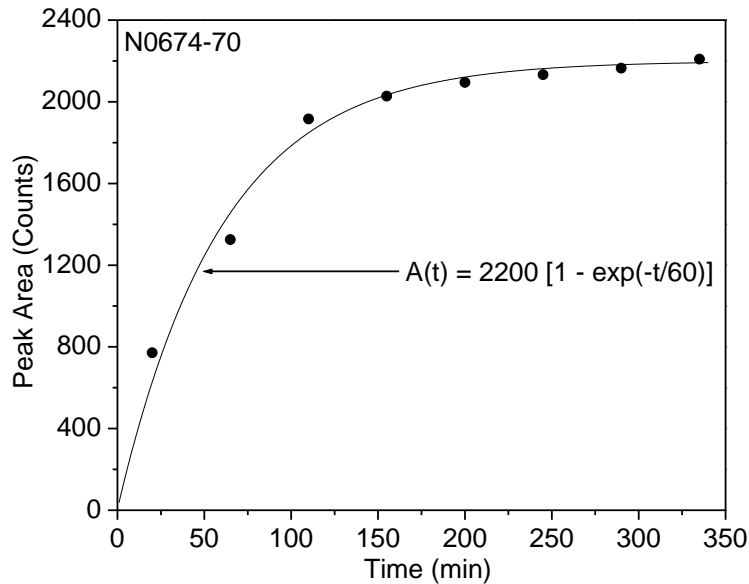


Figure 6: Time variation of the intensity of the line marked by arrow in Figure 5.

4. Experimental Results on Elastomer Swelling

4.1 Comparison of the change in mass and volume

In the inset of Fig. 7, photographs of the two samples before and after treatment with toluene for four hours show significant swelling of the two nitriles. In Fig. 7, percentage increases in the mass and volume of N0674-70 and N0741-75 are plotted as a function of exposure time in toluene. Such large changes made it easier to measure swelling by the simple technique used here. Both samples swell to about twice their size in about 6 hours of exposure with somewhat smaller % increases in mass. Saturation begins to occur after about 8 hours of exposure. On a comparative basis, the peroxide cured nitrile N0741-75 has smaller changes than the nitrile N0674-70 as expected because of the extra cross-linking provided by peroxide curing. Since the density ρ of a material is related to its mass m and volume V by $m=\rho V$, it leads to:

$$(d\rho/\rho) = (dm/m) - (dV/V) \quad (2)$$

From Fig. 7, change in volume dV/V is larger than change in mass dm/m for both samples at a given exposure time in toluene. Using this and equation (2) yields a negative $d\rho/\rho$ meaning that the density of the swelled nitrile is lower or nitrile becomes lighter on exposure to toluene. It is simply due to the fact that toluene is lighter than the elastomers and the diffused toluene lowers the effective density of the swelled elastomers.

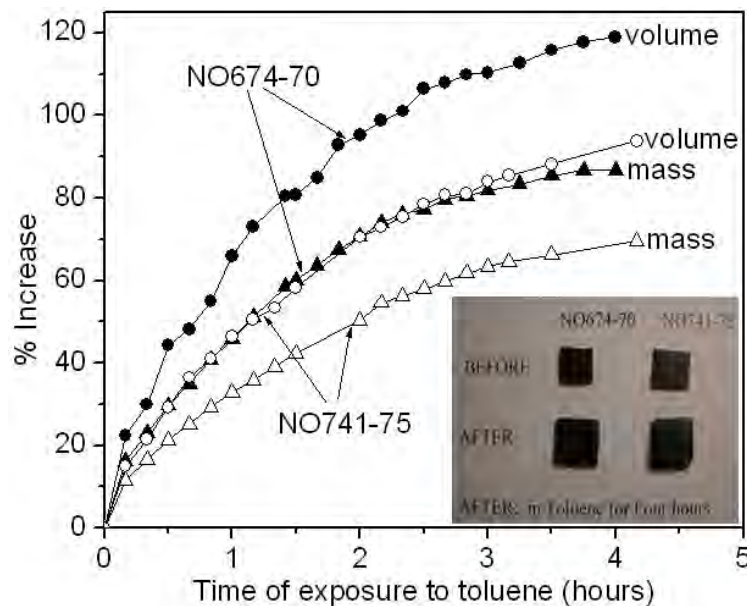


Figure 7: % increase in mass and volume of N0674-70 and N0741-75 vs. time in toluene; the inset shows the photographs of N0674-70 and N0741-75 before and 4hrs after immersion in toluene.

4.2 Time dependence of swelling of elastomer

The long term swelling characteristics of the elastomer N0674-70 in aromatics were investigated. The sample was completely immersed in the solvents, taken out for a few seconds for each measurement at varying times and then put back in the solvents for the next data. This was done for 45 days. The data obtained from the experiments is plotted as percentage change in mass of the elastomer vs. time of immersion in the aromatic solvent, where time is plotted in hours. The swelling trend of the elastomer N0674-70 when immersed in toluene and mesitylene are shown in Fig. 8. The nitrile when immersed in toluene swells to a maximum of about 90% increase in mass, reaching the peak in about 6 hours and then decreases by 4% in about 7 days and then fluctuates around a nearly constant magnitude. Similarly when immersed in mesitylene, the nitrile swells to a maximum of 57% increase in mass, reaching the peak in about 12 hours and then decreases by 4% in about 7 days. As also indicated in the studies by Graham et al [7], the decrease in mass with long-term exposure is likely due to extraction of some part of the fillers by the solvents.

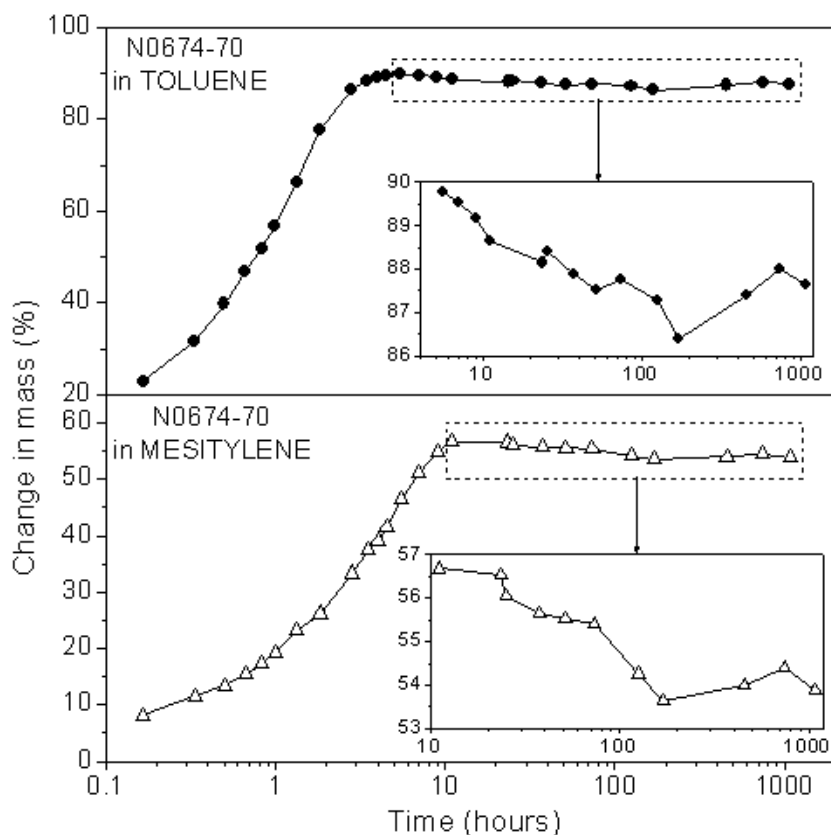
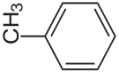
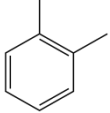
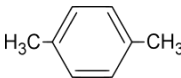
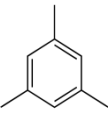
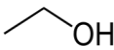

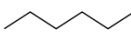


Figure 8: % change in mass vs. time of immersion of NO674-70 in toluene and mesitylene.

4.3 Effect of molar volume of solvent on swelling

To determine the dependence of swelling of elastomer on molecular size of the fluids, swelling of both N0674-70 and N0741-75 in toluene, o-xylene, p-xylene and mesitylene were investigated. As shown in Table 2, these solvents molecules are simple derivatives of benzene but with increasing size and volume.

Table 2: Comparison of molar mass (g/mol), density (g/cm³), molar volume (cm³/mol) of different solvents and the maximum % changes in mass and volume change (%) of nitrile N0674-70 (N0741-75) in different solvents.

	AROMATICS	MOLAR MASS	DENSITY	MOLAR VOLUME	STRUCTURE	Max. MASS CHANGE	Max. VOL CHANGE
1	TOLUENE	92.14	0.867	106.29		90.3 (75.9)	123.7 (101.8)
2	O-XYLENE	106.16	0.88	120.64		86.8 (77.8)	100.5 (94.5)
3	P-XYLENE	106.16	0.861	123.30		73.7 (66.1)	91.5 (81.9)
4	MESITYLENE	120.19	0.864	139.16		56.4 (52.7)	70.3 (68.8)
	ALKANES	MOLAR MASS	DENSITY	MOLAR VOLUME	STRUCTURE	Max. MASS CHANGE	Max. VOL CHANGE
1	ETHANOL	46.07	0.789	58.50		8.9 (8.8)	13.1 (12.7)
2	tert-BUTANOL	74.12	0.7809	94.92		6.5 (6.2)	9.4 (8.7)
3	N-HEXANE	86.18	0.655	131.60		2.9 (4.9)	6.9 (6.8)

In Table 2, the relevant parameters for the four aromatics and three alkanes are listed along with the measured maximum changes in mass and volume for elastomer N0674-70 (N0741-75). In general, the maximum changes in mass and volume are smaller for the peroxide cured nitrile N0741-75. This is expected because of the additional cross linking provided by peroxide curing. Also, the swelling parameters are about an order of magnitude smaller for the alkanes than those for the four aromatics. Within each group, the swelling parameters decrease as the molar volume of the fluid molecule increases.

The three alkanes, ethyl alcohol, tert-butanol and n-hexane, are non-polar molecules and so have only weak chemical interaction with the polar nitrile bond of the elastomers. On the other hand, the aromatics have a polar character and act strongly with the elastomers. Also, the larger molecules diffuse more slowly. So both the chemical interactions and molecular size contribute to the observe swelling of the elastomers.

For the elastomer N0674-70, the percentage changes in mass and volume as a function of square root of time of exposure for the four aromatics are shown in Fig. 9. It is evident that from the graphs that the maximum change in mass and volume of the elastomers is lowered for the larger molecules. To get more quantitative information from this data, plots of $\ln(\text{max. change in volume})$ versus $\ln(\text{molar volume})$ are plotted in Fig. 10(a) for the four aromatics and in Fig. 10(b) for the three alkanes. These plots assume that maximum change in volume, V_{max} , varies with the molar volume of the diffusing species V_{molar} as $V_{\text{max}} \sim (V_{\text{molar}})^{-n}$. For the aromatics $n \approx 2$ is obtained whereas for the alkanes $n \approx 3/4$ is evident.

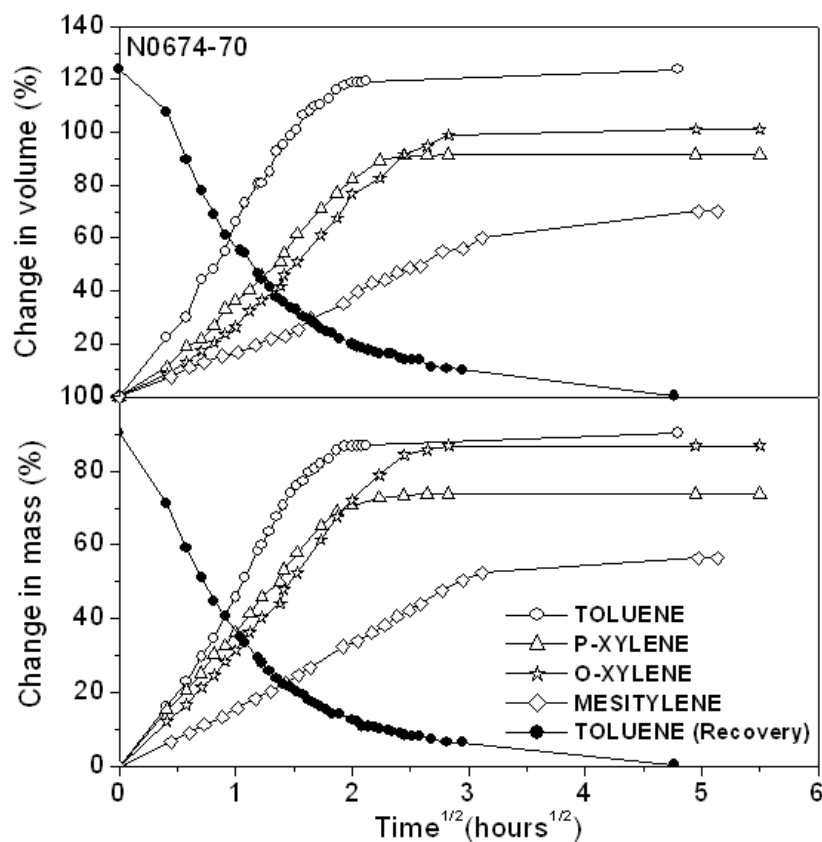


Figure 9: Change in mass and volume percentages vs. $\text{time}^{1/2}$ for nitrile N0674-70 in toluene, p-xylene, o-xylene and mesitylene.

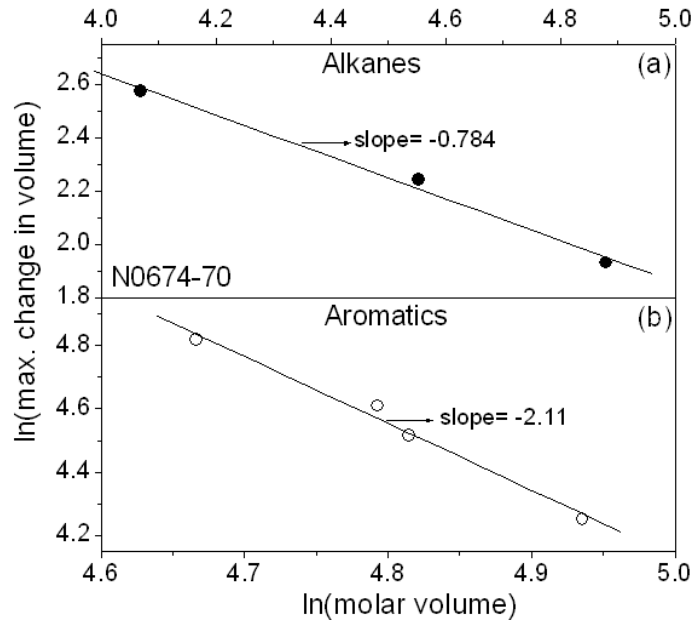


Figure 10: For N0674-70, In-In plots of max. % change in volume vs. molar volume of the four aromatics and three alkanes of Table 2 are shown.

4.4 Recovery mechanism of swelling of elastomers

After the above experiments, the samples were placed in a plastic box exposed to air. When the samples were checked after a few days, it was observed that the elastomers regained their original dimensions suggesting that the swelling process may be completely reversible. The mechanism of recovery was studied as a function of time by removing the swelled nitrile N0674-70 from toluene and exposing it to air. The changes in mass and volume of the sample were measured as a function of time. The results obtained are plotted against the square root of time in Fig. 9 showing complete recovery of the elastomer swelling. These results confirm the findings obtained from the XRD analysis shown in figures 3 through 6.

5. Interpretation of the results

5.1 Diffusion Model

First we invoke diffusion model for the interpretation of swelling of the elastomers in different fluids. Diffusion coefficient, D was calculated using the equation [3, 9, 10]:

$$\frac{t}{\tau} = 1 - \left(\frac{8}{\pi^2}\right) \sum_{n=1}^{\infty} \frac{1}{(2n-1)^2} \exp\left[-\frac{D(2n-1)^2 \tau}{h_0^2}\right] \quad (3)$$

Here Q_t and Q are defined as fractional change in mass at time t relative to $t = \infty$ for Q (saturation) and h_0 is the thickness of the elastomer. For initial times, diffusion of a fluid in an elastomer of thickness h_0 follows the equation [4]:

$$Q_t / Q = 4 (Dt / h_0^2)^n \quad (4)$$

Here $n = 1/2$ for Fickian diffusion for which a plot of (Q_t / Q) vs. $(t^{1/2} / h_0)$ should be linear with the slope $= 4(D / h_0^2)^{1/2}$. This allows determination of D for a given solvent and an elastomer.

As a test of the solution of equation (3) for Fickian diffusion, we first compare normalized mass changes observed in the elastomers N0674-70 when immersed in toluene. In Fig. 11, the experimental variation of the quantity (Q_t / Q) with $(t^{1/2} / h_0)$ is plotted along with the solution of equation (3) as more and more numbers of terms are retained in the infinite series. The effect of higher order terms is only important for very small times as long as about seven terms are retained. For initial times, the data appears to fit the Fickian diffusion. However for later times, the diffusion becomes more rapid resulting in faster saturation than predicted by Fickian diffusion.

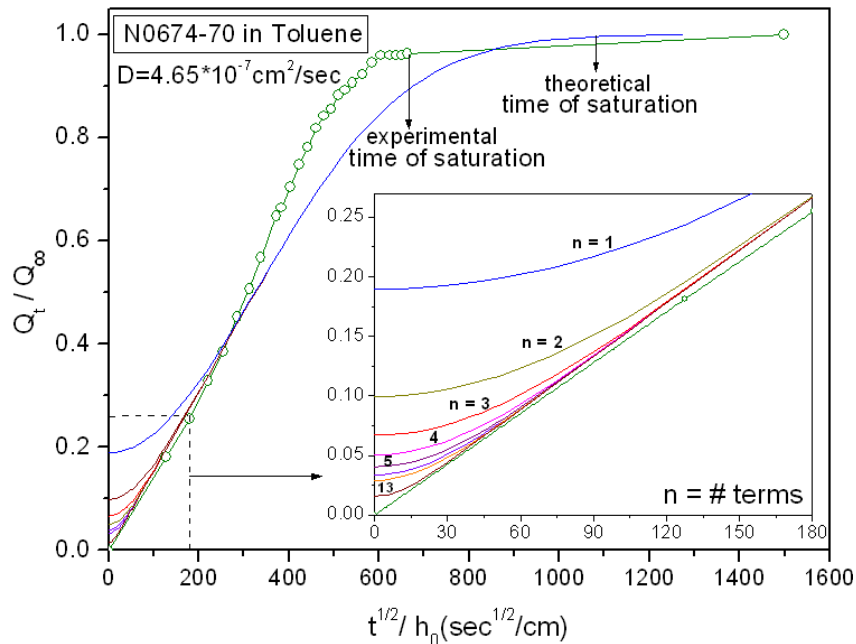


Figure 11: Comparison of the solution of equation (3) with the data on N0674-70 in toluene; the inset gives an expanded view for initial times where $n = \#$ terms retained in the series of Eq. (3).

Assuming that the Fickian law may not be valid for our cases, we fitted the data to the general case of $(Q_t / Q) = kt^n$ which yields:

$$\ln (Q_t / Q_{\infty}) = \ln (k) + n \ln(t) \quad (5)$$

In equation (5), k is a constant that depends on the structural properties of the polymer and gives information about the interaction between polymer and the solvent [4]. The fit of our data to equation (5) is shown in Fig. 12 in the plots of $\ln (Q_t / Q_{\infty})$ vs. $\ln (t)$ with the slope yielding n and the intercept yielding k . The magnitudes of n vary between 0.42 and 0.60 for diffusion of different fluids in N0674-70 and between 0.39 and 0.61 in peroxide cured nitrile N0741-75.

For the case of swelling in toluene, we show the fits of the data to equation (3) as solid line for N0674-70 in Fig. 11. In this case and in all cases investigated in our research, the time t_s to reach saturation determined experimentally are smaller than t_s determined from the fitted curves shown in Fig. 11. This is evident from Fig. 11 where the theoretical fits deviate from the experimental data for larger exposure times. This fact and the fact that n differs from 0.5 suggests that elastomer swelling is not completely Fickian diffusion. Chemical interaction or some other properties of the elastomer and the solvents are also involved.

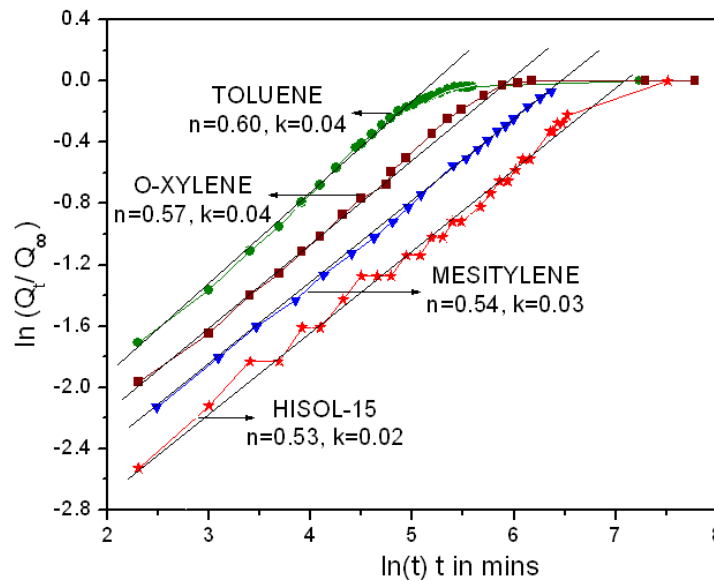


Figure 12: Plots of $\ln (Q_t / Q_{\infty})$ vs. $\ln (t)$ for diffusion of different fluids in N0674-70.

For the elastomer N0674-70, the diffusion constants D_{mass} and D_{vol} (in units of $10^{-7} \text{ cm}^2/\text{sec}$) (D_{mass} is using change in mole percentage and D_{vol} is using change in volume percentage) and n values determined from the initial variations in mass and volume of the elastomers when immersed in the different solvents are shown in Figure 14. The magnitudes of these parameters for the peroxide cured elastomer N0741-75 are shown in Figure 15.

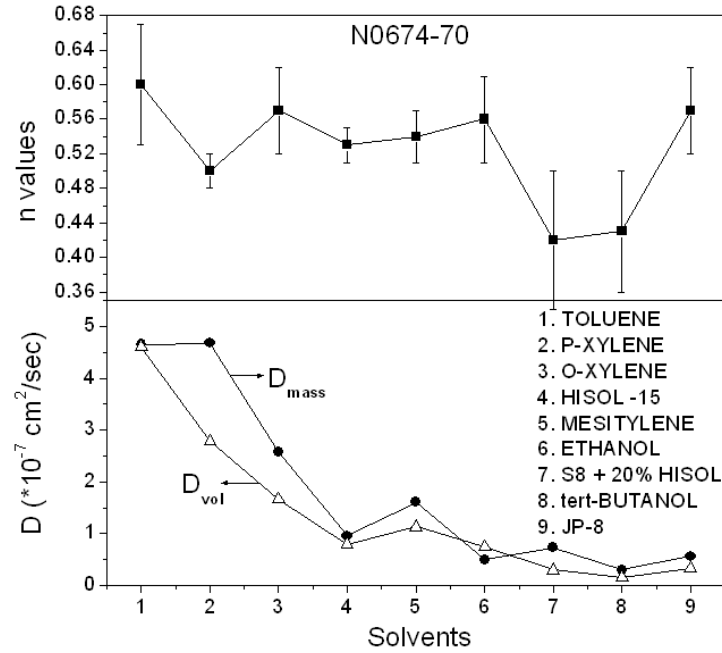


Figure 14: Comparison of D_{mass} , D_{vol} and n values of N0674-70 when immersed in the different solvents.

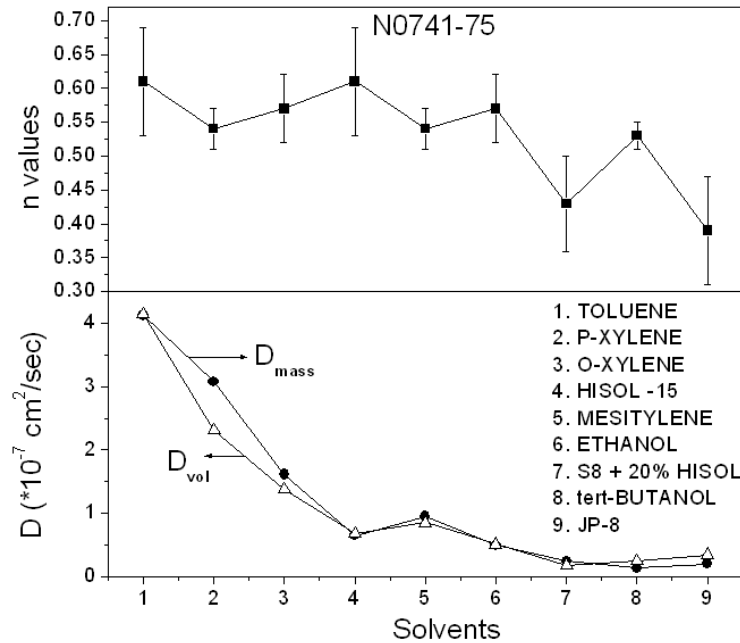


Figure 15: Comparison of D_{mass} , D_{vol} and n values of N0741-75 when immersed in the different solvents.

The main conclusions drawn from the diffusion experiments are as follows:

- Swelling of elastomers in organic fluids occurs by diffusion of the fluid. However it also depends on the properties of the fluid and the elastomer.

- Uptake of the fluids as manifested in changes in mass and volume of the elastomers is larger for N0674-70 than that for the peroxide cured N0741-75. This difference is likely due to extra cross-linking produced by peroxide curing of N0741-75
- Time to reach saturation in swelling varies inversely with D ; larger the D , smaller is the time needed to reach saturation. Mathematically this is also evident from equation (3) since Dt appears in the exponent so that larger D will require fewer terms in the series.
- Percentage change in volume is always larger than percentage change in mass because the density of fluids is less than that of elastomer.
- The diffusion is only approximately Fickian since both the exponent n and the time t_s required for saturation are somewhat different than the prediction of the Fickian diffusion.
- The strength of the interaction of the aromatics (toluene, o-xylene, p-xylene, mesitylene, HISOL-15) with the elastomers is nearly an order of magnitude larger than that of ethanol and tert-butanol. These differences are likely due to the larger hydrogen bonding and polar character of the aromatics [7].

5.2 Hansen Solubility Parameters

Our next effort on the interpretation of the results has been in terms of Hansen Solubility Parameters (HSP's), which are often used for understanding solubility of polymers in solvents. The Hildebrand solubility parameter δ of a fluid is defined in terms of the cohesive energy density (E/V) as:

$$\delta = (E/V)^{1/2} \text{ (cal/cm}^3)^{1/2} \quad (6)$$

where E is the measurable cohesive energy for a molar volume V of a fluid. Hansen extended this concept by showing that contribution to E comes from three separate components: atomic (dispersive) forces E_D , molecular dipolar forces E_P and molecular hydrogen bonding E_H . This leads to [11]:

$$\delta_T^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (7)$$

where $\delta_T^2 = E/V$, $\delta_d^2 = E_D/V$, $\delta_p^2 = E_P/V$ and $\delta_h^2 = E_H/V$. Here δ_d , δ_p and δ_h are the so called Hansen solubility parameters (HSP).

The magnitudes of HSPs for standard solvents and polymers are now available in literature [12]. The magnitudes of HSPs for various solvents used in our work are listed in Table

3 and those of the elastomers with different composition of polyacrylonitrile and polybutadiene are listed in Table 4, the latter based on calculations.

Table 3: Hansen solubility parameters of various solvents.

SOLVENTS		HANSEN SOLUBILITY PARAMETERS			
		δ_T	δ_d	δ_p	δ_h
1	TOLUENE	18.2	18.0	1.4	2.0
2	O-XYLENE	18.0	17.8	1.0	3.1
3	P-XYLENE	17.7	17.4	1.0	3.1
4	MESITYLENE	18.0	18.0	0.0	0.6
5	HISOL-15	17.7	17.4	0.0	3.1
6	JP-8	16.6	16.6	0.2	0.5
7	S-8	16.0	16.0	0.0	0.0
8	ETHYL ALCOHOL	26.5	15.8	8.8	19.4
9	TERT-BUTANOL	21.8	15.2	5.1	14.7
10	N-HEXANE	14.9	14.9	0	0
11	ACETONE	19.9	15.5	10.4	7.0
12	S8 + 20% HISOL	16.3	16.3	0	0.7
13	S8 + 37.5% TOLUENE	16.8	16.8	0.5	0.8

Table 4: Hansen solubility parameters of various elastomers.

ELASTOMERS			HANSEN SOLUBILITY PARAMETERS				
			δ_T	δ_d	δ_p	δ_h	R_o
1	ACRYLONITRILE BUTADINE ELASTOMER		21.0	18.6	8.8	4.2	9.62
2	POLYBUTADINE		18.0	17.5	2.3	3.4	6.55
3	POLYACRYLONITILE		27.4	21.7	14.1	9.1	10.9
	POLYACRYLONITRILE	POLYBUTADIENE					
4	30.0%	70.0%	20.3	18.8	5.8	5.1	
5	34.0%	66.0%	20.7	18.9	6.3	5.3	
6	38.0%	62.0%	21.0	19.1	6.8	5.6	
7	50.0%	50.0%	22.1	19.6	8.2	6.3	

For any elastomer, in a 3D environment, if a sphere is drawn with its HSPs as the center and radius R_o , all the solvents whose HSPs fall within the sphere dissolve the elastomer completely [12]. Using this concept one can identify the solvents which produce the maximum change in volume and mass without performing the immersion tests. However the main difficulty with this approach is the knowledge of R_o accurately which is often determined by measuring the

swelling of the elastomer in a variety of solvents. In Table 4, the calculated magnitudes of the HSPs for different percentages of poly-acrylonitrile and poly-butadiene are listed. In the literature, δ_T listed for standard elastomers is 21.0 which corresponds to 38% poly-acrylonitrile and 62% polybutadiene.

The concept of HSPs for predicting miscibility of solvents and swelling of elastomers is that materials with similar HSPs mix well. Conversely, swelling of polymers in solvents with very different HSPs will be negligible. To quantify this concept for our work, we have plotted the maximum change of volume (swelling) of the two elastomers against the known δ_T for all the solvents used in our work. This comparison for the elastomer N0674-70 is shown in Fig. 16 and for the elastomer N0741-75 in Fig. 17. In both the figures, the data points are fitted to a Gaussian distribution:

$$f(x) = A \exp[-(x-x_0)^2/2\sigma^2] \quad (8)$$

with magnitudes of A , x_0 , and standard deviation σ listed on the figures. Also the position of δ_T for pure polybutadiene, pure polyacrylonitrile and an elastomer made up of 38% polyacrylonitrile and 62% polybutadiene are marked by arrows. These plots provide considerable insight into interpretation of our data as discussed below.

The value of δ_T for n-hexane (≈ 14.9) lies away from that of polybutadiene and the elastomer, and it produces very small change in volume in the elastomer. It is noted that δ_T for pure polybutadiene agrees nearly perfectly with that of toluene ($\delta_T \approx 18.2$), the fluid in which we observe the highest swelling. This is in agreement with our experimental observation that a sample of pure polybutadiene completely dissolves in toluene. The percentage change in volume in elastomer N0674-70 when immersed in acetone ($\delta_T \approx 19.9$) is 112.8% which is a very high swelling percentage. On the other hand, polyacrylonitrile has $\delta_T \approx 27.4$, much higher than those of JP-8 and all solvents used here, making it essentially insoluble in them. Therefore swelling observed in our elastomer can be interpreted to be primarily due to polybutadiene component of the elastomers. Of course, in these comparisons, the role of fillers used in making the elastomer is not taken into account. It has been suggested [2] that the fillers usually dampen the swelling somewhat as they provide strength and prevent complete collapse of the elastomer during swelling. The result that swelling observed in the elastomers may be primarily due to polybutadiene component of the elastomers can be used to design elastomers for desired swelling in a given fluid.

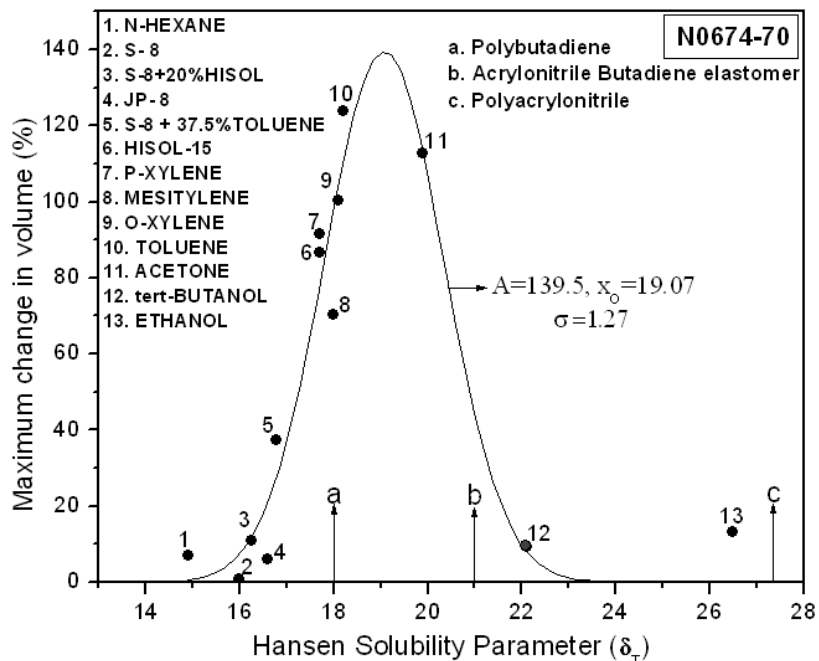


Figure 16: Maximum change in volume (%) of elastomer N0674-70 vs. δ_T .

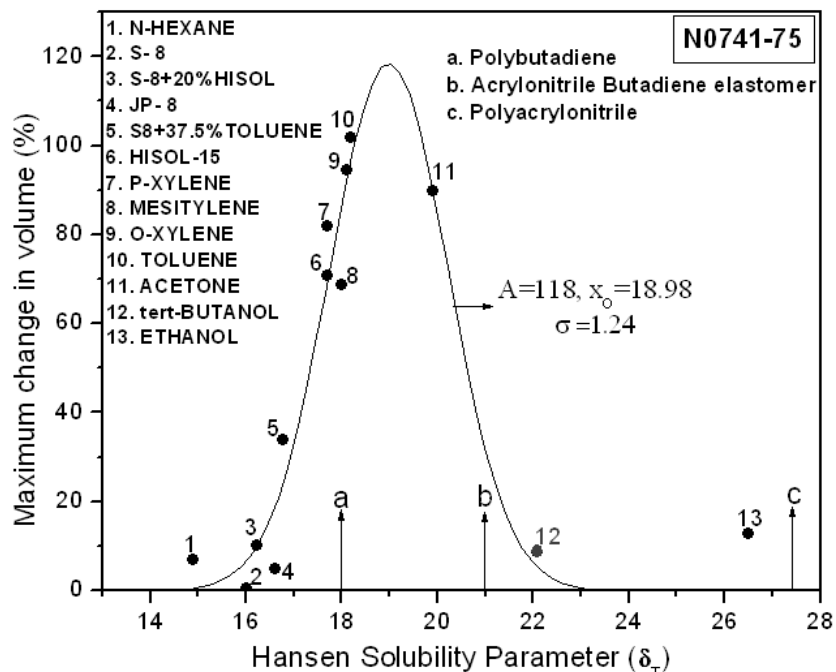


Figure 17: Maximum change in volume (%) of elastomer N0741-75 vs. δ_T .

From the four plots it is observed that the range of δ_T for elastomers for noticeable swelling varies almost like a Gaussian curve starting from $\delta_T = 17$ to $\delta_T = 22$ with maximum swelling occurring near $\delta_T = 19$. Thus knowing δ_T for a solvent, an elastomer can be designed to

meet the desired amount of swelling by varying the percentages of poly-butadiene and poly-acrylonitrile. Conversely, given an elastomer with known δ_T , a solvent with suitable combustion properties can be designed to achieve a given amount of swelling.

6. Discussion and Conclusions

In the results presented above, it has been shown that swelling characteristics of a nitrile in a fluid can be reliably predicted on the basis of the mutual compatibility of their Hansen solubility parameters(HSP's); the closer their HSP's, the higher the swelling. For the synthetic S-5 and S-8 fuels, their HSP of 16.0 differs substantially from that of the nitrile (HSP= 21.0) and consequently swelling of the nitriles in these fuels is quite negligible. On the other hand acetone, which is not an aromatic yet with its HSP = 19.9 due to high polar character of the C=O bond of acetone, produces nearly the same amount swelling of the nitriles as toluene since HSP's of the nitriles and acetone are very close. So aromaticity of a fluid by itself is not a requirement for producing swelling of the nitriles. Other non-aromatic fluids with significant polar character may have compatible HSP's with nitriles. Of course, combustion characteristics of the fluid in a given engine are of great interest in choosing a fluid as an additive to a fuel.

The commercial solvent HISOL-15 which contains mixtures of C9-C11 hydrocarbons with > 98% aromatic content produces nearly 55% swelling of the nitriles. This is due to the closeness of its HSP of 17.7 to that of the elastomers with HSP = 21.0. It is claimed that for HISOL-15, the hazardous air pollutant content is low, sulfur content is very low and its flash point is high (62.8°C).Our experiments show that S8 + 20% HISOL-15 produces about 8% swelling of the two nitriles tested here. So the swelling produced is almost linearly proportional to the amount of HISOL-15 added to S-8. If HISOL-15 is a suitable additive to synthetic fuels from the viewpoint of combustion characteristics, then the above results suggest that a desired amount of swelling of an elastomer can be achieved by mixing appropriate amount of HISOL-15.

On the molecular level, results presented here have shown that diffusion combined with chemical compatibility of the fluid and the elastomer determines the swelling process. The process of diffusion is controlled by the molar volume of the fluid in that the larger molecules have slower diffusion into the nitriles. From the comparison of the HSP's, these studies have established that polybutadiene component of the elastomer provides the swelling whereas the polyacrylonitrile component provides the strength and resistance to swelling. The relative

amounts of these components in an elastomer control its HSP (see Table 6) and hence maximum swelling of the elastomers.

The shrinkage observed after long time exposure is likely due to extraction of the filler material in the nitrile by the fluid since the mass of the sample decreases or due to the escape of the fluid after reaching saturation. What role this shrinkage plays for the eventual failure of the nitriles for sealing purposes was not investigated in this work. For this purpose, really long term (years) exposure and cycling of the elastomer over many cycles is necessary followed by thorough structural characterization of the failed elastomer. It may be speculated that the breakdown of cross-linking and loss of strengthening fillers from the nitriles could lead to elastomer failure.

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